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Stereochemistry of Organic Compounds IX[1)]

On the Optical Contribution of S-Atoms at C_1 and C_6 of Sugars

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We studied the correlation between configuration and optical contribution of sugars[1-6)]. Particularly the chromophores with sulfur atoms indicated a different contribution by the kind of chromophores and the positions of asymmetric centers with the chromophores. For example, the circular dichroism (CD) curves were symmetric between anomers with the xanthyl group at C_1 , and those curves were almost the same between anomers, with the xanthyl group at C_6 .

In the present study, the optical contribution is researched using sugars which introduced sulfur atoms at C_1 and C_6 of sugars. In order to correlate the spectral variations with the S- atoms and O- atoms at C_1 and C_6 of sugars, we newly synthesized the glucosamine derivatives, I, IV, V and VI. We also investigated the detailed comparisons of the compounds, II[3)], III[5)], VII[7)], VIII[7)] and IX[6)].

All the compounds that we have examined are illustrated in Fig. 1.

Results and Discussion

In Figure 2, the rotatory dispersion (RD), CD and ultraviolet absorption (UV) curves of compounds I, II and III are shown. The data of CD and UV is given in

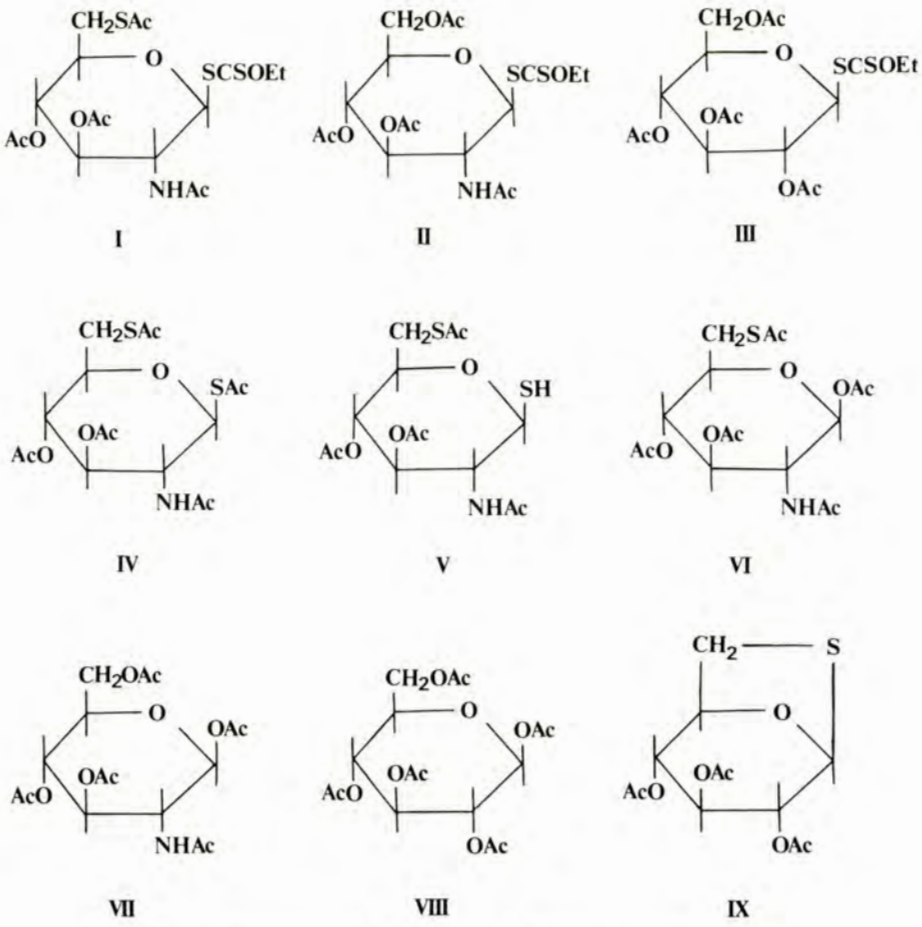


Fig. 1 Structures of Derivatives of Glucoses and Glucosamines

Table 1. The results show that the compound II has the largest optical contribution and the compound III has the smallest. This means that the first band, due to the $n \rightarrow \pi^*$ transition, is weakened by S−atom at C_6 , and strengthened by −NHAc group at C_2 . The curvature of the CD and UV curves were the same and the signs of Cotton effects are the same, positive, negative and positive from the long wavelength. Therefore the configurations around the bands are similar. In the case of glucoses with the chromophore like xanthyl groups, the results show that the −NHAc group at C_2 contributes positively and the sulfur atom contributes negatively, but they don't cause the direction of the transition moment to change.

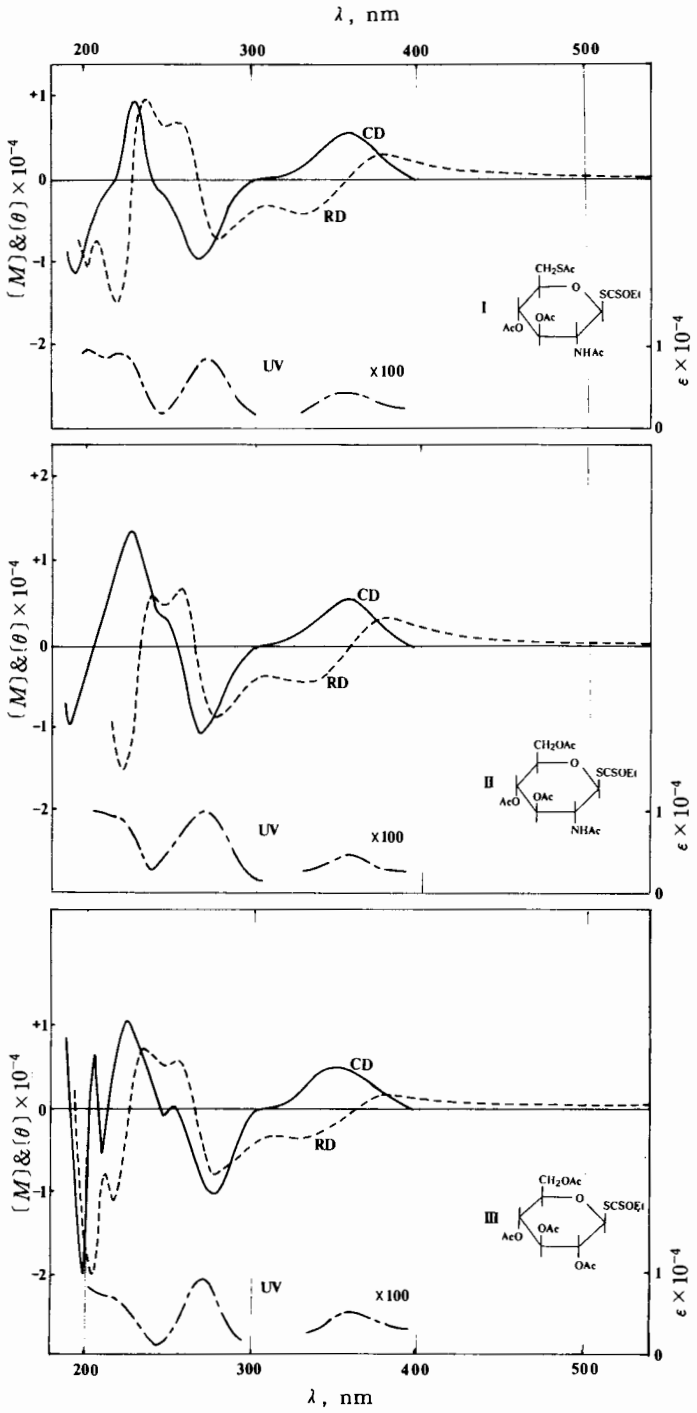


Fig. 2 RD, CD and UV of Compounds I–III (in ethanol)

Table 1 CD and UV Data of Compounds I—III (in ethanol)

Comp.	CD			UV		
	Band 1 $[\theta]$ (λ, nm)	Band 2 $[\theta]$ (λ, nm)	Band 3 $[\theta]$ (λ, nm)	Band 1 $[\varepsilon]$ (λ, nm)	Band 2 $[\varepsilon]$ (λ, nm)	Band 3 $[\varepsilon]$ (λ, nm)
I	+5380 (358)	−9940 (270)	+9270 (230)	40.8 (358)	8430 (274)	8980 (222)
II	+5860 (358)	−10600 (270)	+13900 (228)	47.3 (358)	10200 (272)	9190 (220)
III	+2720 (356)	−10400 (268)	+10800 (227)	33.2 (360)	9240 (272)	7040 (216)

Table 2 CD, UV and $[M]_{589}$ Data of Compounds IV—IX (in ethanol)

Comp.	CD		UV			RD
	Band 1 $[\theta]$ (λ, nm)	Band 2 $[\theta]$ (λ, nm)	Band 1 ε (λ, nm)	Band 2 ε (λ, nm)	Band 3 ε (λ, nm)	$[M]_{589}$
IV	+1040 (266)	— (below 200)	12.0−41.4 (326−292)	8890 (227)		−210
V	− 383 (274)	−11800 (207)	15.6−49.1 (296−270)	3920 (228)		−3.72
VI	−70.1 (285)	+280 (256)	11.2−56.4 (378−312)	370−668 (298−266)	4440 (227)	−45.4
VII	+ 558 (222)		8.50−8.81 (261−253)			+93.4
VIII	+ 704 (222)		15.0−16.2 (271−252)	316 (206)		+6.36
IX	−2880 (243)		43.1−75.4 (257−244)			−305

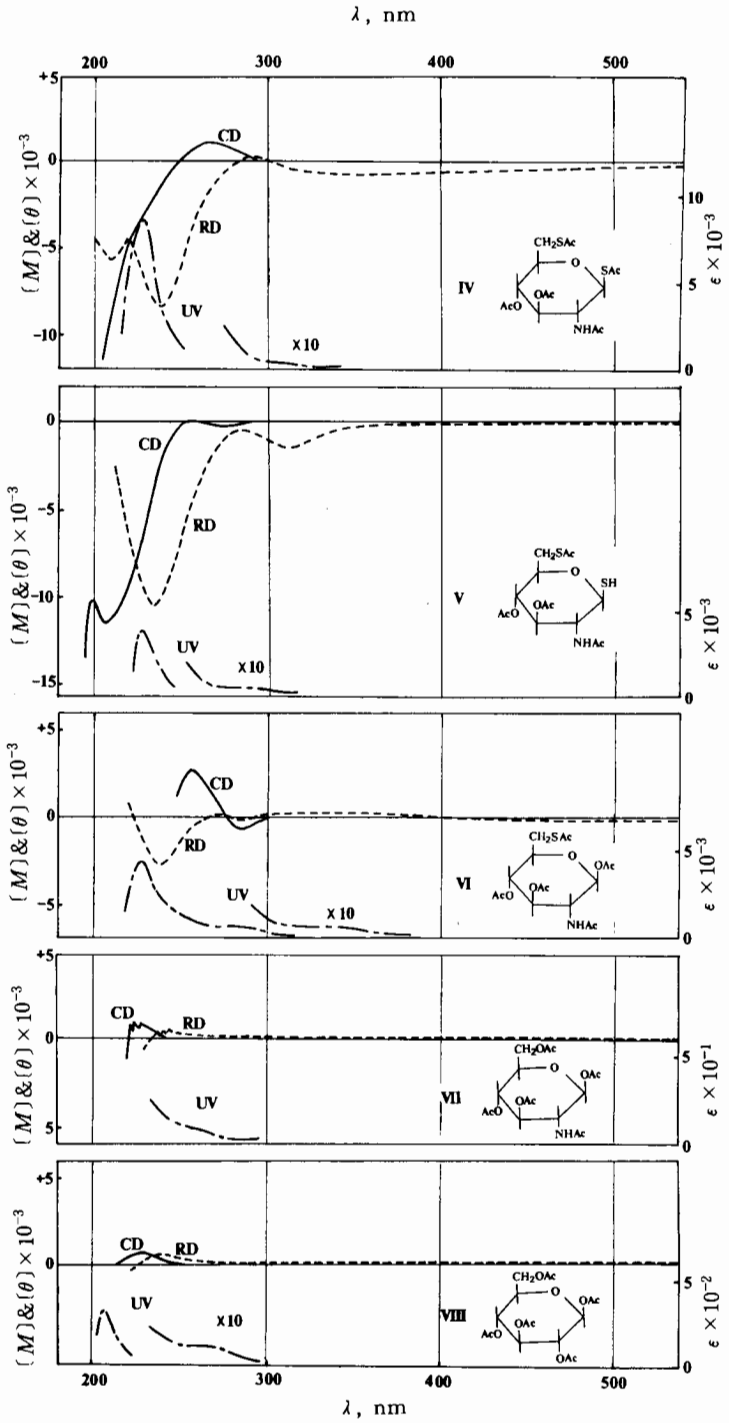


Fig. 3 RD, CD and UV of Compounds IV–VIII (in ethanol)

In Figure 3, we show the RD, CD and UV curves of compounds IV−VIII. And the RD, CD and UV curves of the compound IX are given in Fig. 4. The data of CD, UV and RD for compounds IV−IX is given in Table 2.

Now looking at the values of $[M]_D$ in Table 2, the compounds VII and VIII with the −OAc group at C_6 show positive values. The compounds IV, V and VI with the −SAc group at C_6 show negative values.

From this we understand that the sulfur atom at C_6 contributes negatively, in the long wavelength region apart from the wavelength of the absorption band. These results are in harmony with the results in compound I. Next we can focus on the CD curves in Figs. 3 and 4. The CD curve of compound IV shows a positive extreme at 266 nm and suggests strongly negative extreme below 200 nm. The pattern of the CD curves for compound IV is almost the same as in the compounds VII and VIII. But the sulfur atom bathochromically shifted about 40 nm[8]. The CD curve of compound V shows a slight negative extreme at 274 nm and a strongly negative at 207 nm. In the case of the compound VI, two Cotton effects were observed at 285 nm in the negative and at 256 nm in the positive. These Cotton effects corresponded to the Cotton effects at 274 nm in the compounds IV and at 266 nm in V. Therefore, this leads us to believe that the Cotton effect around 270 nm

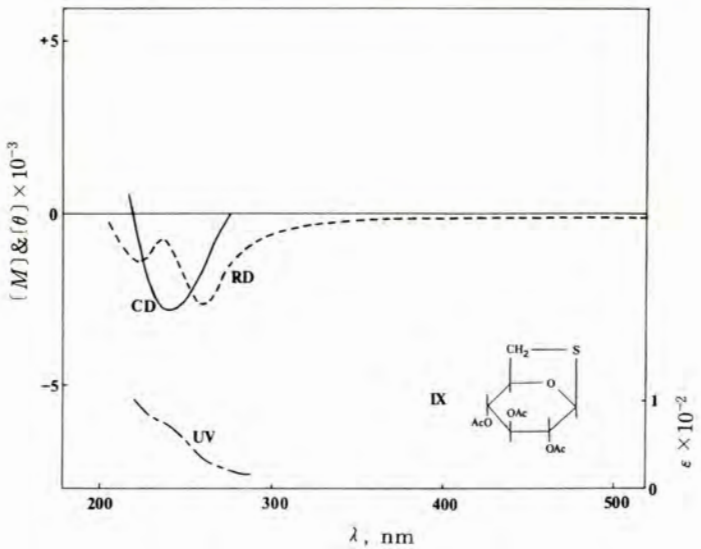
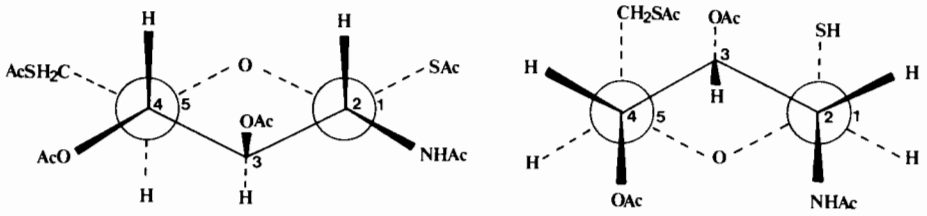


Fig. 4 RD, CD and UV of Compound IX (in ethanol)

in IV and V split into two Cotton effects in the compound VI.

From these results we conclude that the compounds IV, VII and VIII have the same conformation which have the largest repulsion between the same groups, −SAc, at C_1 and at C_6 . This makes the C1 conformation. In the case of the compound V, there is an interaction between the SH group at C_1 and the SAc group at C_6 . As a result these two groups are close and the 1C conformation is predominant.

The compound VI has the distorted form which is derived from the C1⇌1C equilibrium. In Figure 5, the preferable conformations of the compounds IV and V using the Newman's projection are illustrated.



IV V

Fig. 5 Newman's projections of Compounds IV and V

The compound IX has the bridged S atom, therefore, the sugar moeity can take only the 1C conformation. The compound V shows the negative Cotton effect at 243 nm, and the shapes of the CD curves of compounds V and IV are symmetrical.

We can now discuss the assignment of absorption bands. In the compounds I, II and III, the first Cotton effect is due to the $n\rightarrow\pi^*$ transition of C=S, judging from the energy level. In the compounds IV, V and VI, there is a possibility of the charge transfer within −SAc group, whereas, in the compound IX, which doesn't have π electrons around sulfur atom, the Cotton effect observed was the same as the compounds IV, V and VI. Therefore it may be considered that, in the compounds IV, V, VI and IX, the Cotton effects at 240−270 nm are due to the $n\rightarrow\sigma^*$ transition.

This transition occurs from a nonbonding orbitals between sulfur and carbon atoms[10, 11].

References

1) K. Satsumabayashi, Y. Nomoto and H. Nakahara, This Bulletin, **6**,83 (1977).
2) Y. Tsuzuki, K. Tanaka and K. Satsumabayashi, *Bull. Chem. Soc. Japan*, **35**, 1614 (1962).
3) Y. Tsuzuki, K. Satsumabayashi, M. Akagi and S. Tejima, *ibid.*, **37**,162 (1964).
4) Y. Tsuzuki, K. Tanaka, K. Satsumabayashi, M. Akagi and S Tejima, *ibid.*, **37**,730 (1964).
5) K. Satsumabayashi, Y. Nishida and H. Nakahara, This Bulletin, **6**,83 (1977); **7**,137 (1978).
6) K. Satsumabayashi and Y. Nishida, *ibid.*, **8**,119 (1978).
7) K. Satsumabayashi and Y. Nishida, *ibid.*, **13**,85 (1984).
8) H. Meguro, E. Ohtaki, K. Tuzimura, N.A. Hughes and Leslie Hough, *Tetrahedron lett.*, **36**,3371 (1978).
9) B. Ringdahl, J.C. Craig and A. Fredga, *Acta Chem. Scand.* B **35**,507 (1981).
10) P.M. Scopes, R.N. Thomas and M.B. Rahman, *J. Chem. Soc.* (C), 1671 (1971).
11) J.S. Rosenfield and A. Moscowitz, *J. Am. Chem. Soc.*, **94**,4797 (1972).